Supporting Information

Well-Defined Liquid Crystal Gels from Telechelic Polymers

Yan Xia, Rafael Verduzco, Robert H. Grubbs, Julia A. Kornfield

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Experimental

General Procedures. NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. All NMR spectra were recorded in $CDCl_3$ or DMSO-d_6, and referenced to residual proteo species. For end group analysis, a Varian Mercury 500 MHz ^{1}H NMR was used. FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 5μm mixed-C columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and d*n*/d*c* values were obtained for each injection by assuming 100% mass elution from the columns.

Materials. Dichloroethane (DCE) was dried over CaH_2 and distilled prior to use. *trans*-5,6-dihydroxy-cyclooctene[1], and 5-hydroxy-cyclooctene[2] were synthesized according to literature procedures. All other materials were used as received.

Synthesis of functionalized cyclooctene-based monomers. Ethyl 6-bromohexanoate (19.8 mL, 111 mmol) was attached to 4-cyano-4′-hydroxybiphenyl

(15.4g, 78.9 mmol) in anhydrous DMF (100 mL) with anhydrous K_2CO_3 (10.8 g, 78.1 mmol) at 90 °C for 6 h. The product was recrystallized in ethanol (89% yield), and was then deprotected by reacting with KOH (6 g, 150 mmol) in anhydrous ethanol (200 mL) at 90 °C for 6 h. 1 M HCl (50 mL) was added to precipitate the acid product which was collected by filtration, washed with water and cold acetone, and dried in vacuo at 60 °C (95% yield).

The acid (5.2 g, 16.2 mmol) was reacted in $SOCl_2$ (60 mL, 766 mmol) at 70 °C for five hours to convert into the acid chloride. Excess $SOCl_2$ was removed under reduced pressure. The acid chloride was then dissolved in 20 ml anhydrous THF and was added dropwise to a solution of *trans*-5,6-dihydroxy-cyclooctene (0.77 g, 5.4 mmol) in anhydrous pyridine (5 mL, 63.2 mmol) and anhydrous THF (50 mL). The mixture was refluxed for 24 h and the product was purified by extraction with 1 N HCl (20 mL, 3 times), followed by extraction with a saturated solution of aqueous $NaHCO_3$ (50 mL) and with a saturated aqueous solution of KCl (50 mL). The product was dried over MgSO4 and purified on a silica gel column (ethyl acetate/hexanes, 3:7 v/v) to give 1.6 g disubstituted cyclooctene **1** as a white crystal (40% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.60 (m, 8H), 7.52-7.49 (m, 4H), 6.97-6.94 (m, 4H), 5.64 (t, J = 4.2 Hz, 2H), 5.18 (t, J = 3.3 Hz, 2H), 3.98 (t, J = 6.3 Hz, 4H), 2.52-2.00 (m, 12H), 1.85-1.45 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 159.6, 145.2, 132.6, 131.4, 128.7, 128.3, 127.0, 119.5, 115.0, 109.5, 73.7, 67.7, 34.3, 29.9, 28.9, 25.7, 24.7, 23.0. HRMS (FAB) *m/z* calc. for $C_{46}H_{48}O_6N_2$: 724.3522, found 724.3512.

Monosubstituted cyclooctene **2** was synthesized in analogy to **1** by coupling the acid chloride with 5-hydroxy-cyclooctene (65% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ

7.71-7.62 (m, 4H), 7.55-7.50 (m, 2H), 7.00-6.95 (m, 2H), 5.73-5.57 (m, 2H), 4.88-4.80 (m, 1H), 4.00 (t, J = 8.1 Hz, 2H), 2.38-2.07 (m, 6H), 1.92-1.50 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 159.7, 145.3, 132.6, 131.3, 129.8, 129.6, 128.3, 127.1, 119.1, 115.0, 110.0, 75.5, 67.8, 34.6, 33.8, 33.7, 28.9, 25.6, 25.5, 24.8, 24.7, 22.3. HRMS (FAB) *m/z* calc. for $C_{27}H_{31}O_3N$: 417.2304, found 417.2294.

Synthesis of 1,8-dibromo-4-octene. 5-Bromo-1-pentene (1.0 g, 6.7 mmol) was added to a solution of Grubbs 1st generation catalyst (30 mg, 0.036 mmol) in 5 ml degassed CH_2Cl_2, and the reaction stirred at room temperature overnight. The solvent was evaporated and the remaining residual was purified on a silica gel column (ethyl ether/hexanes, 1:20 v/v) to give 0.80 g 1,8-dibromo-4-octene (89% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45-5.37 (m, 2H), 3.43-3.38 (m, 4H), 2.24-2.12 (m, 4H), 1.96-1.86 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.8, 129.3, 33.3, 32.5, 32.2, 30.8, 25.7. HRMS (FAB) *m/z* calc. for $C_8H_{14}Br_2$: 269.9442, found 269.9455.

General procedure for polymerization and end group functionalization. In a typical experiment, an oven-dried small vial was charged with 0.725 g (1.0 mmol) of monomer **1** and a stir bar. Under an argon atmosphere, 1.0 ml of degassed DCE was added via syringe. The vial was then degassed through three freeze-pump-thaw cycles. Next, the desired amount of CTA was injected from its stock solution in degassed DCE. 84 μl of a 10.0 mg/ml Grubbs 2nd generation catalyst solution in degassed DCE was injected to initiate the polymerization. The reaction vial was stirred at 55 °C under argon for 24 h. The reaction mixture was quenched with 0.1 ml of ethyl vinyl ether and then dissolved in 2 ml CH_2Cl_2 and precipitated into 200 ml stirring MeOH. The pale yellow

precipitate was washed with fresh MeOH and dried in vacuo overnight to yield 0.70 g of white polymer (97% yield).

0.7 g (0.1 mmol -Br) dibromo-terminated polymer and 13 mg (0.2 mmol) NaN_3 were dissolved in 15 ml DMF. The resulting solution was stirred at 25 °C overnight and then concentrated and precipitated into 200 ml MeOH three times and dried in vacuo overnight to yield 0.65 g light yellow polymer (93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7-7.6 (m, 8H), 7.6-7.5 (m, 4H), 7.0-6.9 (m, 4H), 5.4-5.3 (br, 2H), 5.1-5.0 (br, 2H), 4.05-3.9 (br, 4H), 3.3-3.2 (m, end group -C*H*$_2$-N_3), 2.4-2.3 (m, 4H), 2.2-1.45 (br m, 20H).

Diazido-terminated polymer **4** was synthesized from monomer **2** using a similar procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7-7.6 (m, 4H), 7.6-7.5 (m, 2H), 7.0-6.9 (m, 2H), 5.4-5.3 (br, 2H), 4.95-4.8 (br, 1H), 4.05-3.95 (br, 2H), 3.3-3.2 (m, end group -C*H*$_2$-N_3), 2.4-2.3 (m, 2H), 2.2-1.2 (br m, 16H).

General procedure for crosslinking. The desired diazido-terminated polymer and CuBr (2 eq. to alkyne) were added to a small vial with a Teflon-lined cap. The vial was evacuated and backfilled with argon three times. The desired amount of degassed, anhydrous DMF (resulting in a 25 wt % polymer solution) and pentamethyl diethylene triamine (PMDETA) (1 eq to CuBr) were injected and the vial was stirred for 5 min. The correct amount of tripropargylamine (1/3 eq to polymer azide end group) was then injected from its stock solution. The mixture was stirred at room temperature for 20 seconds. The vial was then placed in an oven preset to 50 °C and allowed to react for 2 days. The resulting gels were repeatedly extracted with DMF and then THF (2 h for each extraction and for 1-2 days until the solution was visually colorless) to remove copper catalyst and soluble polymer fraction. Upon drying in vacuo, the material returns to the

light yellow color of the prepolymer. The elastomer films for electro-optic studies were prepared by injecting the reaction mixture into rectangular glass cells with predetermined gaps. This was required for preparing samples of a uniform thickness. A cell was sealed in a degassed vial with a Teflon-lined cap. After injecting the reaction mixture into the rectangular cell, the vial was placed in a heating oven at 50 ^{o}C. After 2 days at 50 °C, the glass cell was soaked in DMF for several hours and opened carefully to remove the gel. The catalyst and soluble polymer fraction was extracted as described above. The gel was then dried in vacuo and the resulting film was reswelled with 5CB for 24 h to give the LC gel film.

Electro-optic measurements of the gels. The electro-optic properties of the gels were measured under oscillating applied voltage using a polarized He-Ne laser, a beam splitter, and a CCD detector as previously described.[3] Constrained samples were prepared by pressing a LC gel sample between indium-tin-oxide (ITO)-coated quartz plates separated by 10-μm spacers. Unconstrained samples were prepared by placing a thin (~40 μm, measured using an outside micrometer by gently placing the gel between the anvil and the spindle) piece of the LC gel in a 100 μm-thick gap between ITO and lecithin coated glass plates filled with 5CB, and the samples were allowed to stand overnight to allow full alignment of 5CB before measurements.

Spectra and Electro-optic Measurements

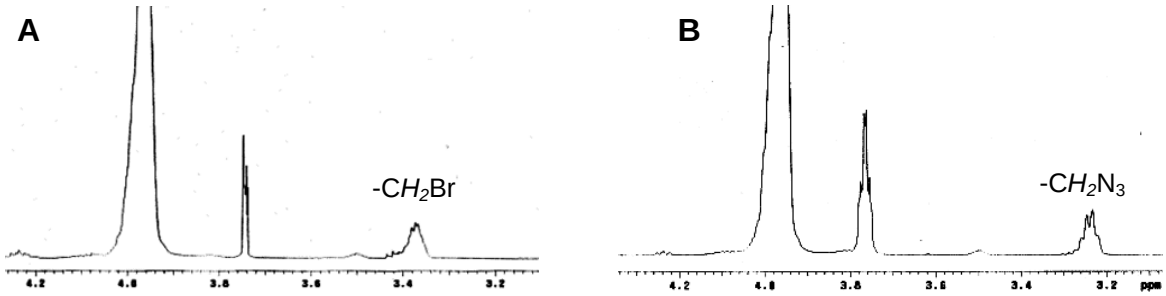

Figure 1S. ^{1}H NMR spectra (zoom of region 3.1-4.2 ppm) of polymer **3** isolated from polymerization (A) and after NaN_3 treatment (B).

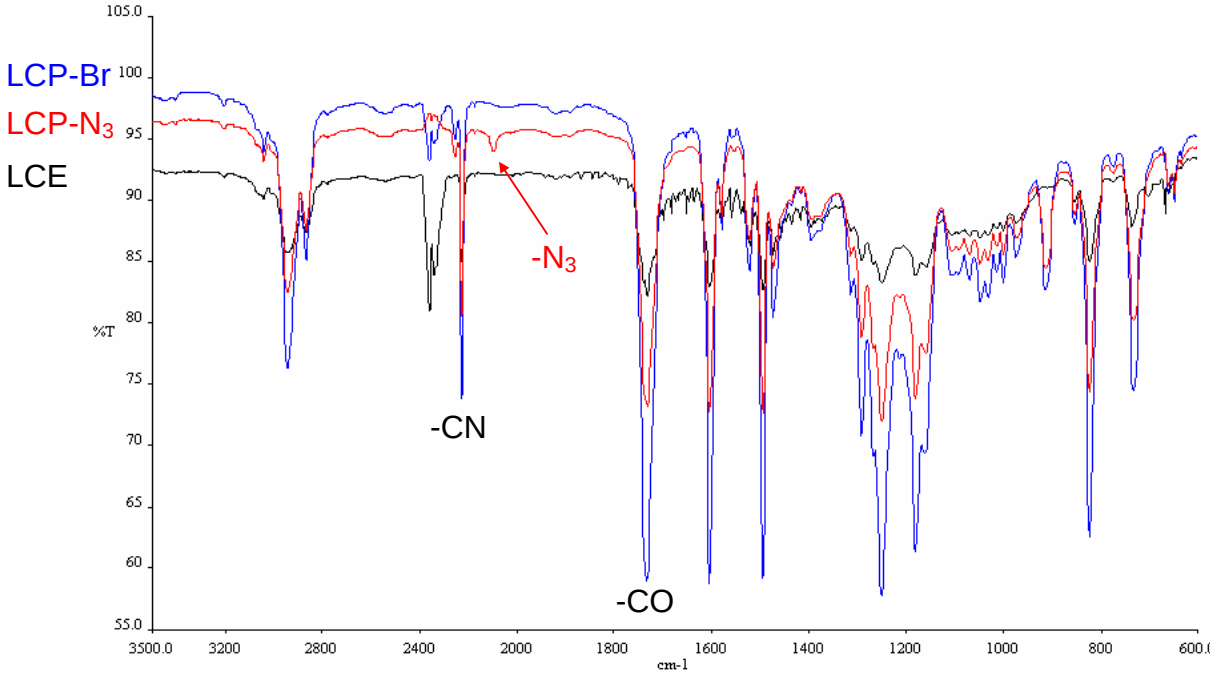

Figure 2S. IR spectra of polymer **3** isolated from polymerization (top), after NaN_3 treatment (middle), and after crosslinking at acetylene:azide=1:1 (bottom).

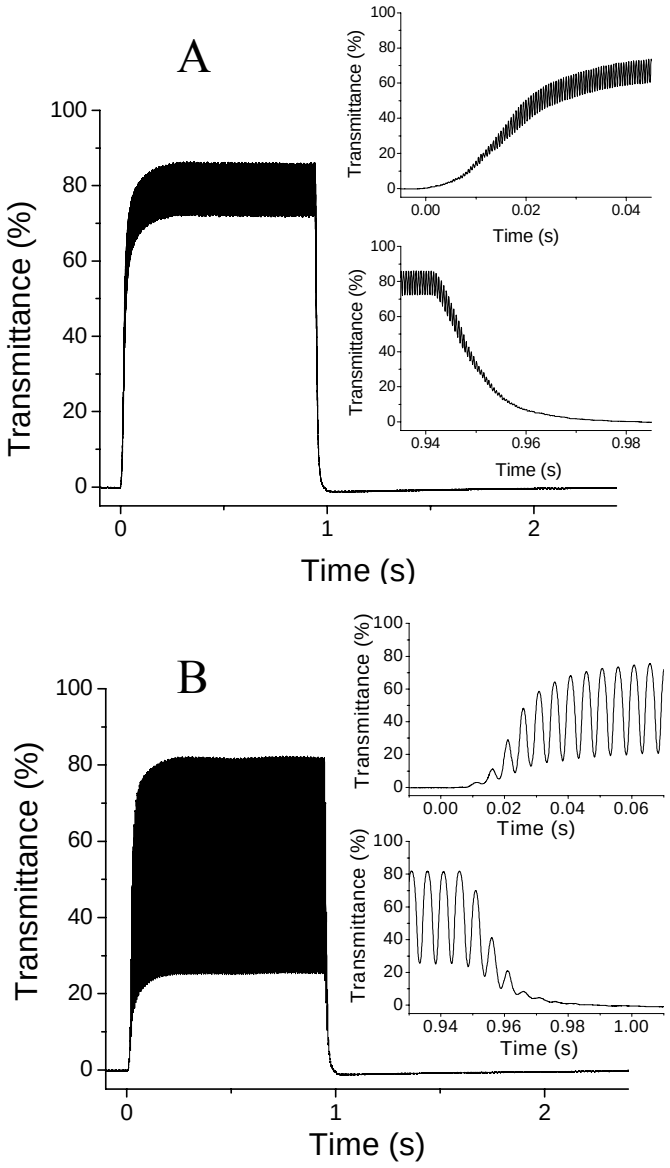

Figure 3S. Transient electro-optic response of an unconstrained LC gel (LCG2) under an AC electric field of 2.0 V/μm at A) 1000 Hz, B) 100 Hz. The insets show the electro-optic response around the time the signal is applied (top inset) and removed (bottom inset).

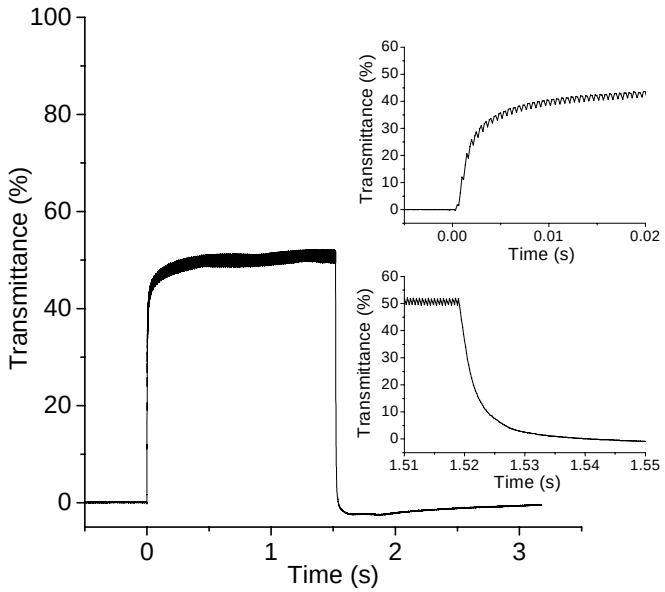

Figure 4S. Transient electro-optic response of an unconstrained LC gel (LCG1) under an AC electric field of 2.0 V/μm at 1000 Hz. The insets show the electro-optic response near the time the signal is applied (top inset) and removed (bottom inset).

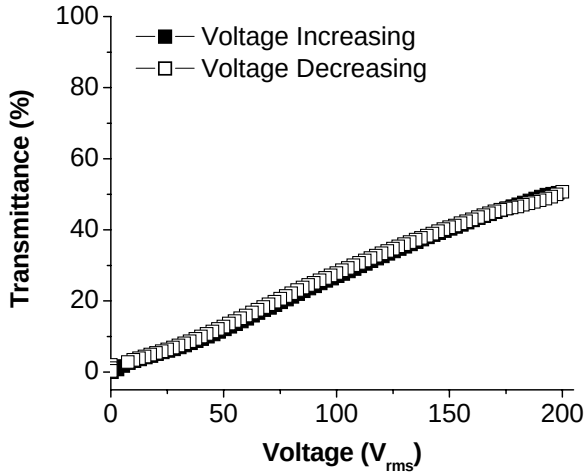

Figure 5S. Transmittance as a function of voltage applied for an unconstrained LC gel (LCG1) in a 100 μm-thick gap. The applied AC voltage (rms) sweeps from 0 to 200V at 0.5V interval and 1000 Hz.

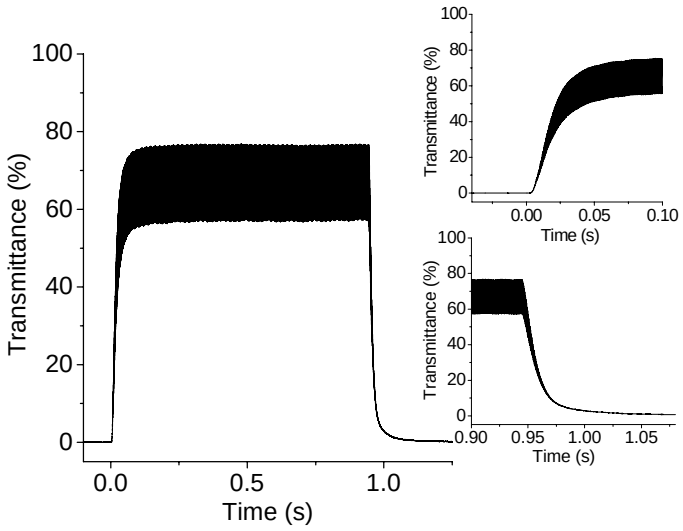

Figure 6S. Transient electro-optic response of an unconstrained LC gel (monosubstituted LCG3) under an AC electric field of 2.0 V/μm at 1000 Hz. The insets show the electro-optic response near the time the signal is applied (top inset) and removed (bottom inset).

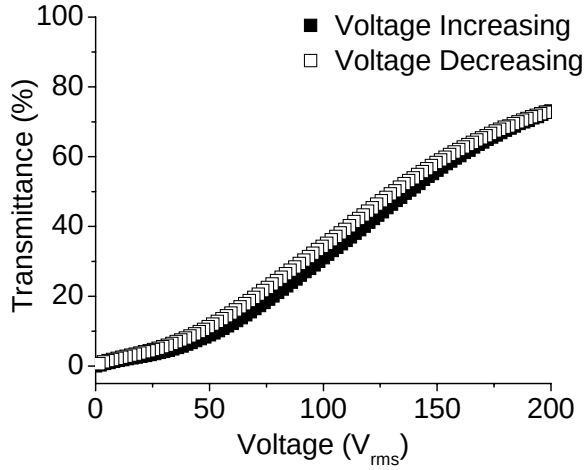

Figure 7S. Transmittance as a function of voltage applied for an unconstrained LC gel (LCG3) in a 100 μm-thick gap. The applied AC voltage (rms) sweeps from 0 to 200V at 0.5V interval and 1000 Hz.

References

(1) Jernow, J. L.; Gray, D.; Closson, W. D. *J. Org. Chem.* **1971**, *36*, 3511-3515.

(2) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311-6316.

(3) Kempe, M. D.; Scruggs, N. R.; Verduzco, R.; Lal, J.; Kornfield, J. A. *Nature Materials* **2004**, *3*, 177-182.